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CONFERENCE ON pH MEASUREMENTS

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CONFERENCE ON pH MEASUREMENTS

[Following is a translation of an article by M. A. Portnov in Meditsinskaya Promyshlennost' SSSR (Medical Industry of the USSR), No, 2, Moscow, 1950.]

The quantity pH is gaining an ever increasing importance in science, technology, and agriculture.

The pH measurement is of an exceptionally great significance in the automation of control procedures for continuous processes in the chemical and the chemico-pharmaceutical industries.

At the conference on pH measurements, 27 to 31 October 1959, in Tbilisi, 250 delegates participated and 35 reports on the most vital problems in the theory and applications of pH measurements were heard.

Corresponding member of the Academy of Sciences USSR, Professor B. P. Nikol'skiy gave a report on "The Theoretical Foundations of pH Measurements" and outlined a program for the most important work to be done in the area of thermodynamics of solutions in relation to the theory and practice of pH measurements.

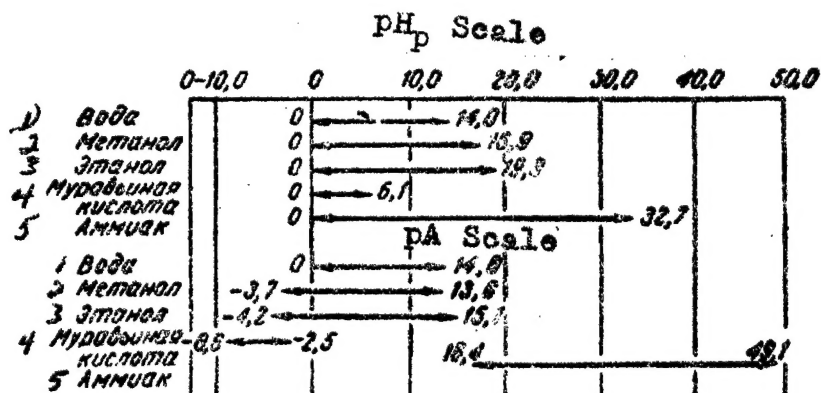


Fig. 1. Comparison of acidity scales pH_p and pH.

1) water; 2) methanol; 3) ethanol, 4) formic acid; 5) ammonia.

Corresponding member of the Academy of Sciences Ukrainian SSR, Professor N. A. Izmaylov, reported on the results of work on measurements of acidity in non-aqueous solutions. One should note that Professor N. A. Izmaylov's work on the creation of a unified acidity scale is of a particular importance. Figure 1 points out the data for water, methanol, ethanol, ammonia, and formic acid.

The upper part of Fig. 1, the so-called pH_p scale, characterizes the distinct ranges in conformity with the ion product of the various solvents with an arbitrarily chosen common zero point for all of the solvents.

The lower part of the diagram (pA scale) correlates within a single scale the acidities in various solvents in relation to a standard, namely, the proton activities in an infinitely dilute aqueous solution, and in this case the range of the single scale is essentially changed (in the given case from -8.6 to +49.1) and it comprises almost 10 units instead of 14 (0 to +14) pH units for an aqueous system.

A considerable number of the reports were devoted to the theory and application of glass electrodes for pH measurements in aqueous and non-aqueous solvents: M. M. Shul'ts (Leningrad State University), A. M. Aleksandrova (Khar'kov State University), M. L. Kurskaya (NIOPiK), Z. I. Tsutskiridze (SKB PSA), M. A. Portnov (VNIKhFI named after S. Ordzhonikidze), G. S. Bogdanova (Glass Institute), A. N. Khutsishvili (SKB PSA) and others.

What are the basic results of the work on this very important problem of pH measurements?

1. Establishment of a program for scientific and experimental work on glass compounding and on the technology of glass making as well as on the manufacture of glass and auxiliary electrodes suitable in a wide pH range (0 - 14) and at elevated temperatures (to 100°) in order to enable a quick organization of serial production of glass and auxiliary electrodes.

2. Electrode cells of various designs suitable for periodical and continuous pH measurements under industrial conditions at temperatures up to 100° and at pressures to 0.5 atm. have been developed (Ts L A of the Ministry of Construction RSFSR, SKB PSA - Tbilisi).

3. The block-type pH-meter PVU 5056 developed at

TsLA by A. S. Benevol'skiy (Fig. 2) was found to be suitable for a continuous automatic control of the pH as found by state testing (report by M. A. Zemel'man, representing the All-Union Scientific Research Institute's Committee of Standards, Measures, and Measuring Instruments).

The conclusions on the quality of the pH-meter PVU 5056 have been corroborated during a three-month testing program at the chemico-pharmaceutical plant n. a. Karpov and conducted by VNIKhFI n. a. S. Ordzhonikidze under industrial conditions.

The Lenteplopribor plant has started serial production of TsLA's pH-meters (according to information given by representative of the plant, P. F. Shmidt).

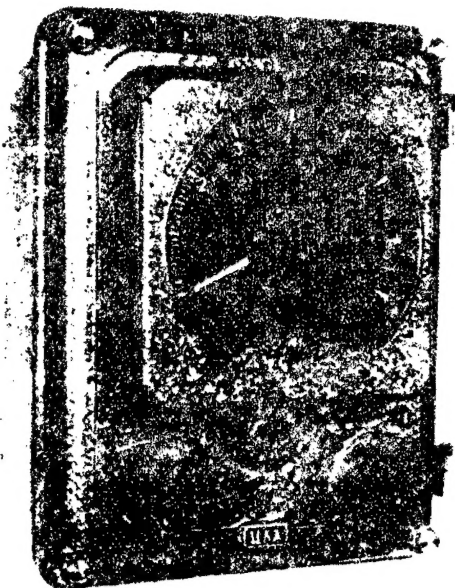


Fig. 2. Automatic block-type pH-meter TsLa.

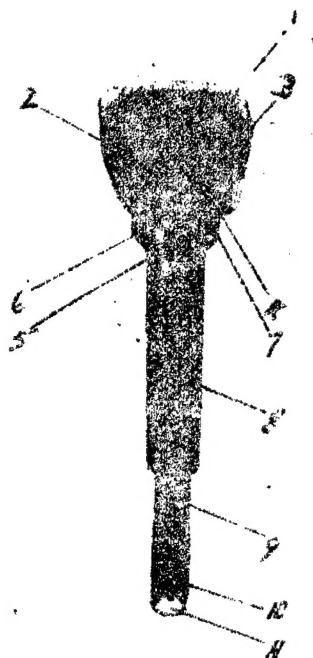


Fig. 3. Portable rod-type pH-meter SKB PSA.

- 1) microammeter M - 24; 2) controls for zero adjustment;
- 3) temperature compensator control; 4) needle corrector;
- 5) collar of the head; 6) scale selector slit; 7) range selector slit; 8) instrument shaft housing the feeder batteries; 9) pick-up cell with a protective cover; (10) and a removable beaker (11).

For a periodical pH measurement under industrial conditions the portable rod-type pH-meter PShP (Fig. 3) developed by SKB PSA (Tbilisi) is fully adequate. Its accuracy of measurement is within the limits of $\pm 0.1 - 0.2$ pH units in the range from pH 2 to 12. The instrument is immersible. It has a glass and a silver - silver chloride electrode system. The instrument is fed by dry elements and there is no fire hazard. Serial production of the instrument has been started by instrument-building plants of the Council of National Economy of the Georgian SSR.

For pH measurements under laboratory and field conditions the so-called agro-chemical pH-meters with a scale and accuracy of the rod-type pH-meters can be used (developed by the Skb of Instrument-Building and Automation Means in Tbilisi).

Regrettably, at the conference there were no reports on new developments in precision pH measurements under laboratory conditions, and, apparently, there is no unique organization capable to meet to some extent the needs of scientific and industrial laboratories until such time that the Moskip plant will make its appearance with the tube-type potentiometers LP - 5 and LP - 57.

There was a report by engineer V. P. Yukhnovskiy (TsLA) on a new type of a block pH-meter (PVU - 5080) suitable for measurements with an accuracy of ± 0.05 pH units under industrial conditions.

Valuable reports were given by Professor P. A. Kryukov, N. V. Peshekhonovaya, and others on the application of glass electrodes with metallic functions; such an application makes it possible to speed up considerably the determination of a series of cations (e.g. sodium in native water and in industrial solutions, potassium ions and others).

On a new, highly promising type of electrodes made of ion-exchange resins (membrane electrodes) there was a report by Ye. A. Materova (Leningrad State University).

The authors pointed out a practical feasibility for the creation of electrodes made of ion-exchange resins, reversible not only for H^+ , but also for other ions (Na^+ , K^+ , Li^+ , NH_4^+ , Ag^+ , Ba^{++} , Ca^{++} , Br^- , Cl^- , F^-).

Application of such electrodes can considerably simplify and speed up methods of analysis and control of chemical processes which is of a great practical importance for many branches of the national economy and also for the chemico-pharmaceutical industry among others.

Of a great practical interest in a number of cases is the application of metallic-oxide electrodes, particularly when not too great an accuracy is required (± 0.4 pH units in a series), when mechanical conditions or aggressiveness of the medium does not permit the use of glass electrodes.

To this type of electrodes were devoted a number of reports (A. A. Shcherbakov, Anfimov, M. A. Portnov, O. F. Klyuchko, and others).

In the report by the representative of VNIKhFI a possibility of the use of technical antimony of the Su - 0 grade for making of electrodes was shown. This would considerably simplify the technology of metal preparation for the casting of electrodes. Furthermore, a description of

the structure of a pick-up cell for continuous automatic pH control as well as data on continuous operation of a pH-meter - standard automatic potentiometer set were given.

As the most important problem in practical pH measurements one must consider the development of methods of standardization of measurements, establishment of standard pH values and systems of control. To these problems a number of reports were devoted (All-Union Scientific Research Institute for Metrology imeni D. I. Mendeleev, Khar'kov State University, SKB PSA). Report by V. V. Aleksandrov (Khar'kov State University) on standardization of the pH scale in aqueous solutions at various temperatures presents a theoretical as well as a practical interest. Having compared the methods of standardization in various countries and characterized the basic chemical and physico-chemical properties of compounds suitable for buffer solutions the speaker pointed out the basic causes for errors and possible ways for their elimination.

The resolution of the conference contained a project for putting an end to the lag in the industrial-technical basis in the field of pH measurements in relation to the requirements of industry and agriculture.

With the aim to coordinate the work in the field of pH measurements and to eliminate the duplication of work within various organizations the conference recommended the establishment of a scientific-technical council for pH measurements under the Council of Ministers' State Committee for Machine Building and Automation on which organizations working mainly in the field of pH measurements would be represented, among them also the VNIKhFI n. a. S. Ordzhonikidze.

Introduction of progressive technology in the chemico-pharmaceutical industry must be accompanied by the introduction of the latest methods of automatic control and particularly, as practice has shown, of the pH measurement.

In line with the general technical requirements of the chemico-pharmaceutical industry there is also the specific condition that the pH meters be workable under industrial conditions: a wide spectrum of organic solvents, elevated temperatures (to 130°) and pressures to 5 atm.

To satisfy the needs of the chemico-pharmaceutical industry it is necessary that the Ministry of Health USSR (with the participation of scientific-research and planning institutions) and industrial enterprises formulate

within the shortest possible time their requirements of the instrument-building organizations in regard to the quality of the pH-meters, specific operating conditions (temperature, pressure, corrosive conditions, non-flammability, and non-explosiveness) as well as determine their needs in instruments up to the end of the seven-year period.

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